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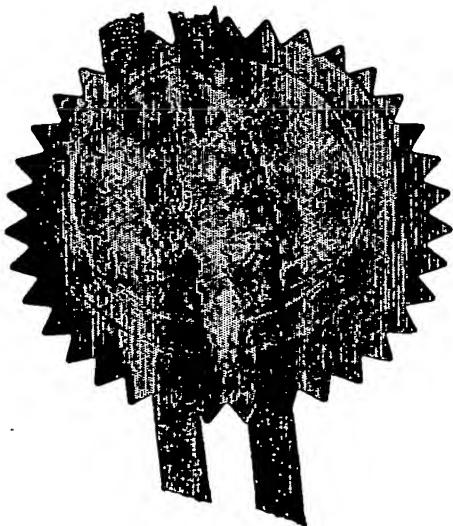
PCT

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21MAR03 E793924-1 C03022
P01/7700 0.00-0306430.0

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1. Your reference

9998

2. Patent application number

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0306430.0

20 MAR 2003

3. Full name, address and postcode of the or of each applicant (*underline all surnames*)

BP CHEMICALS LIMITED
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UNITED KINGDOM

Patents ADP number (*if you know it*)

4141891002

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention

POLYMERISATION AND OLIGOMERISATION CATALYSTS

5. Name of your agent (*if you have one*)

HAWKINS, David George

"Address for service" in the United Kingdom to which all correspondence should be sent
(including the postcode)

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UNITED KINGDOM

Patents ADP number (*if you know it*)

4030177002

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Country

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Number of earlier application

Date of filing
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YES

- a) *any applicant named in part 3 is not an inventor, or*
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Patents Form 1/77

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Claim(s) -

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Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

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11.

I/We request the grant of a patent on the basis of this application.

Dave Hawkins
Signature
HAWKINS, David George

Date 20th March 2003

12. Name and daytime telephone number of person to contact in the United Kingdom

(01932) 763366

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POLYMERISATION AND OLIGOMERISATION CATALYSTS

The present invention relates to transition metal-based polymerisation and oligomerisation catalysts and to their use in the polymerisation, copolymerisation and oligomerisation of olefins.

The use of certain transition metal compounds to polymerise 1-olefins, for example, ethylene or propylene, is well established in the prior art. The use of Ziegler-Natta catalysts, for example, those catalysts produced by activating titanium halides with organometallic compounds such as triethylaluminium, is fundamental to many commercial processes for manufacturing polyolefins. Over the last three decades, advances in the technology have led to the development of Ziegler-Natta catalysts which have such high activities that olefin polymers and copolymers containing very low concentrations of residual catalyst can be produced directly in commercial polymerisation processes. The quantities of residual catalyst remaining in the produced polymer are so small as to render unnecessary their separation and removal for most commercial applications. Such processes can be operated by polymerising the monomers in the gas phase, or in solution or in suspension in a liquid hydrocarbon diluent, or, in the case of propylene in bulk.

Commodity polyethylenes are commercially produced in a variety of different types and grades. Homopolymerisation of ethylene with transition metal based catalysts leads to the production of so-called "high density" grades of polyethylene. These polymers have relatively high stiffness and are useful for making articles where inherent rigidity is required. Copolymerisation of ethylene with higher 1-olefins (eg butene, hexene or octene) is employed commercially to provide a wide variety of copolymers

differing in density and in other important physical properties. Particularly important copolymers made by copolymerising ethylene with higher 1-olefins using transition metal based catalysts are the copolymers having a density in the range of 0.91 to 0.93.

These copolymers which are generally referred to in the art as "linear low density polyethylene" are in many respects similar to the so called "low density" polyethylene produced by the high pressure free radical catalysed polymerisation of ethylene. Such polymers and copolymers are used extensively in the manufacture of flexible blown film.

Polypropylenes are also commercially produced in a variety of different types and grades. Homopolymerisation of propylene with transition metal based catalysts leads to the production of grades with a wide variety of applications. Copolymers of propylene with ethylene or terpolymers with ethylene and higher 1-olefins are also useful materials, often used in film applications.

In recent years the use of certain metallocene catalysts (for example 15 bis(cyclopentadienylzirconiumdichloride activated with alumoxane) has provided catalysts with potentially high activity. Other derivatives of metallocenes have been shown to be potentially useful for producing polypropylene with good activity, molecular weight and tacticity control. However, metallocene catalysts of this type suffer from a number of disadvantages, for example, high sensitivity to impurities when 20 used with commercially available monomers, diluents and process gas streams, the need to use large quantities of expensive alumoxanes to achieve high activity, difficulties in putting the catalyst on to a suitable support and synthetic difficulties in the production of more complex catalyst structures suitable for polymerising propene in a tactic manner.

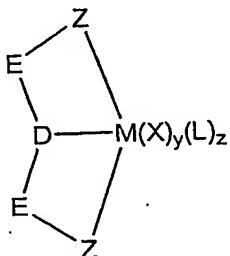
Olefin oligomerisation is also a commercially important process, leading to the 25 production of 1-olefins (1-hexene, 1-octene, 1-decene, etc) that find utility in a wide range of applications, for example as comonomers for linear low density polyethylene, monomers for poly(1-olefins) and starting materials for surfactants. Catalysis based on a wide range of metal complexes may be used for this process and typically produce a 30 so-called "Schultz-Flory" distribution of 1-olefins. More recently catalysts have emerged that selectively produce only 1-hexene by a distinctive trimerisation mechanism. Typically the final distribution of 1-olefins produced is of importance

commercially.

An object of the present invention is to provide a catalyst suitable for polymerising or oligomerising monomers, for example, olefins, and especially for polymerising or oligomerising ethylene alone or propylene alone, or for copolymerising ethylene with higher 1-olefins with high activity. A further object of the invention is to provide an improved process for the polymerisation of olefins. Yet another object of the present invention is to provide novel complexes based on certain transition metals. The catalysts described here show extremely high activity for polymerisation and oligomerisation which leads to many benefits including lower catalyst loadings in a commercial process and lower catalyst residues in nay final product.

The present invention provides a novel polymerisation catalyst comprising

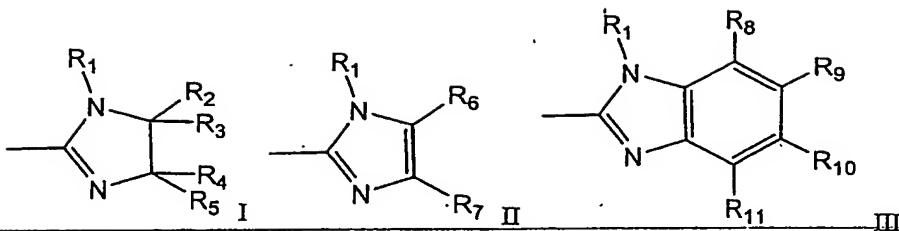
- (1) a transition metal compound having the following Formula A, and optionally
- (2) an activating quantity of a suitable activator,



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wherein Z is specifically an imidazole-containing group; M is a metal from Group 3 to 7 of the Periodic Table or a lanthanide metal; E is a divalent group independently selected from (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups and (vi) heterosubstituted derivatives of said groups (i) to (v); D is a donor group; X is an anionic group, L is a neutral donor group; y and z are independently zero or integers such that the number of X and L groups satisfy the valency and oxidation state of the metal M.

Concerning the imidazole-containing group Z, this is suitably a group of formula I, II or III



R_1 to R_{11} are independently hydrogen or a monovalent (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), and (vii) hydrocarbyl-substituted heteroatom groups. These defined groups preferably contain 1 to 30, more preferably 2 to 20, most preferably 2 to 12 carbon atoms. Examples of suitable aliphatic hydrocarbon groups are methyl, ethyl, ethylenyl, butyl, hexyl, isopropyl and tert-butyl. Examples of suitable alicyclic hydrocarbon groups are adamantyl, norbornyl, cyclopentyl and cyclohexyl. Examples of suitable aromatic hydrocarbon groups are phenyl, biphenyl, naphthyl, phenanthrenyl and anthacenyl. Examples of suitable alkyl substituted aromatic hydrocarbon groups are benzyl, toyl, mesityl, 2,6-diisopropylphenyl and 2,4,6-triisopropyl. Examples of suitable heterocyclic groups are 2-pyridinyl, 3-pyridinyl, 2-thiophenyl, 2-furanyl, 2-pyrrolyl, 2-quinolinyl. Suitable substituents for forming heterosubstituted derivatives of said groups R_1 to R_{11} are, for example, chloro, bromo, fluoro, iodo, nitro, amino, cyano, ether, hydroxyl and silyl, methoxy, ethoxy, phenoxy (i.e. $-OC_6H_5$), tolyloxy (i.e. $-OC_6H_4(CH_3)$), xylyloxy, mesityloxy, dimethylamino, diethylamino, methylethylamino, thiomethyl, thiophenyl and trimethylsilyl. Examples of suitable heterosubstituted derivatives of said groups (i) to (v) are 2-chloroethyl, 2-bromocyclohexyl, 2-nitrophenyl, 4-ethoxyphenyl, 4-chloro-2-pyridinyl, 4-dimethylaminophenyl and 4-methylaminophenyl. Examples of suitable hydrocarbyl-substituted heteroatom groups are chloro, bromo, fluoro, iodo, nitro, amino, cyano, ether, hydroxyl and silyl, methoxy, ethoxy, phenoxy (i.e. $-OC_6H_5$), tolyloxy (i.e. $-OC_6H_4(CH_3)$), xylyloxy, mesityloxy, dimethylamino, diethylamino, methylethylamino, thiomethyl, thiophenyl and trimethylsilyl. Any of the substituents R_1 to R_{11} may be linked to form cyclic structures. Substituents R_2 to R_{11} may also suitably be inorganic groups such as fluoro, chloro, bromo, iodo, nitro, amino, cyano and hydroxyl.

Further suitable imidazole-containing groups may be obtained by removal of substituent R₁, for example by deprotonation when R₁ is hydrogen, to give formally monoanionic imidazole-containing groups.

It is preferred that the imidazole-containing group has a structure described in formula III (a "benzimidazole"). R₁ is preferably hydrogen, an aliphatic hydrocarbon group, an aromatic hydrocarbon group or is removed to give a formally monoanionic benzimidazole group. R₈ to R₁₁ are preferably hydrogen, an aliphatic hydrocarbon group or an aromatic hydrocarbon group.

E is independently selected from divalent (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), and (vii) hydrocarbyl-substituted heteroatom groups. Examples of suitable divalent group R₅ are -CH₂- , -CH₂CH₂- , -CH₂CH₂CH₂- , 1,2-phenylene, *trans*-1,2-cyclopentane, *trans*-1;2-cyclohexane, 2,3-butane, 1,1'-biphenyl, 1,1'-binaphthyl, and -Si(Me)₂- . It is preferred that E is an aliphatic or aromatic hydrocarbon group. More preferably E is -CH₂CH₂- .

D is a donor group, for example oxygen, sulfur, an amine, an imine or a phosphine. Preferably D is oxygen, sulfur, an amine of formula -N(R₁₂)- or a phosphine of formula -P(R₁₃)- wherein R₁₂ and R₁₃ are hydrogen or (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), (vii) hydrocarbyl-substituted heteroatom groups and (viii) further imidazole-containing groups. Alternatively R₁₂ or R₁₃ may be removed, for example by deprotonation when they are hydrogen, to give a formally monoanionic fragments. More preferably D is an amine of formula -N(R₁₂)- as defined above. R₁₂ is preferably hydrogen, an aliphatic hydrocarbon, an aromatic hydrocarbon or a further imidazole containing group.

M is preferably a metal selected from Groups 3 to 7 of the periodic table, more preferably selected from Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn and most preferably V and Cr.

The anionic group X can be, for example, a halide, preferably chloride or bromide; or a hydrocarbyl group, for example, methyl, benzyl or phenyl; a carboxylate, for example, acetate or acetylacetate; an oxide; an amide, for example diethyl amide; an

alkoxide, for example, methoxide, ethoxide or phenoxide. Alternatively, X can be a non-coordinating or weakly-coordinating anion, for example, tetrafluoroborate, a fluorinated aryl borate or a triflate. The anionic groups X may be the same or different and may independently be monoanionic, dianionic or trianionic.

5 The neutral donor group L can be, for example, a solvate molecule, for example diethyl ether or THF; an amine, for example, diethyl amine, trimethylamine or pyridine; a phosphine, for example trimethyl phosphine or triphenyl phosphine; or an olefin.

10 The value of y depends on the formal charge on each group Z and D, the charge on the anionic group X and the oxidation state of the metal M. For example, if M is chromium in oxidation state +3, both Z groups are neutral and D is neutral, then y is 3 if X is a monoanionic group (e.g. chloride); if M is chromium in oxidation state +3, one Z group is neutral, one Z group is monoanionic and D is neutral, then y is 2 if all X groups are monoanionic groups (e.g. chloride).

15 The optional activator (2) for the catalyst of the present invention is suitably selected from organoaluminium compounds and organoboron compounds or mixtures thereof. Additional Suitable organoaluminium compounds include trialkylaluminium compounds, for example, trimethylaluminium, triethylaluminium, tributylaluminium, tri-n-octylaluminium, ethylaluminium dichloride, diethylaluminium chloride and alumoxanes. Alumoxanes are well known in the art as typically the oligomeric 20 compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic or mixtures thereof. Commercially available alumoxanes are generally believed to be mixtures of linear, cyclic and cage compounds. The cyclic alumoxanes can be represented by the formula $[R^{16}AlO]_s$ and the linear alumoxanes by the formula 25 $R^{17}(R^{18}AlO)_s$ wherein s is a number from about 2 to 50, and wherein R^{16} , R^{17} , and R^{18} represent hydrocarbyl groups, preferably C₁ to C₆ alkyl groups, for example methyl, ethyl or butyl groups.

30 Examples of suitable organoboron compounds are dimethylphenylammoniumtetraphenylborate, trityltetraphenylborate, triphenylboron, dimethylphenylammonium tetra(pentafluorophenyl)borate, sodium tetrakis[(bis-3,5-trifluoromethyl)phenyl]borate, $H^+(OEt_2)[(bis-3,5-trifluoromethyl)phenyl]borate$, trityltetraphenylborate and

tris(pentafluorophenyl) boron. Mixtures of organoaluminium compounds and organoboron compounds may be used.

In the preparation of the catalysts of the present invention the quantity of activating compound selected from organoaluminium compounds and organoboron compounds to be employed is easily determined by simple testing, for example, by the preparation of small test samples which can be used to polymerise small quantities of the monomer(s) and thus to determine the activity of the produced catalyst. It is generally found that the quantity employed is sufficient to provide 0.1 to 20,000 atoms, preferably 1 to 2000 atoms of aluminium or boron per atom of M present in the compound of Formula A. Mixtures of different activating compounds may be used.

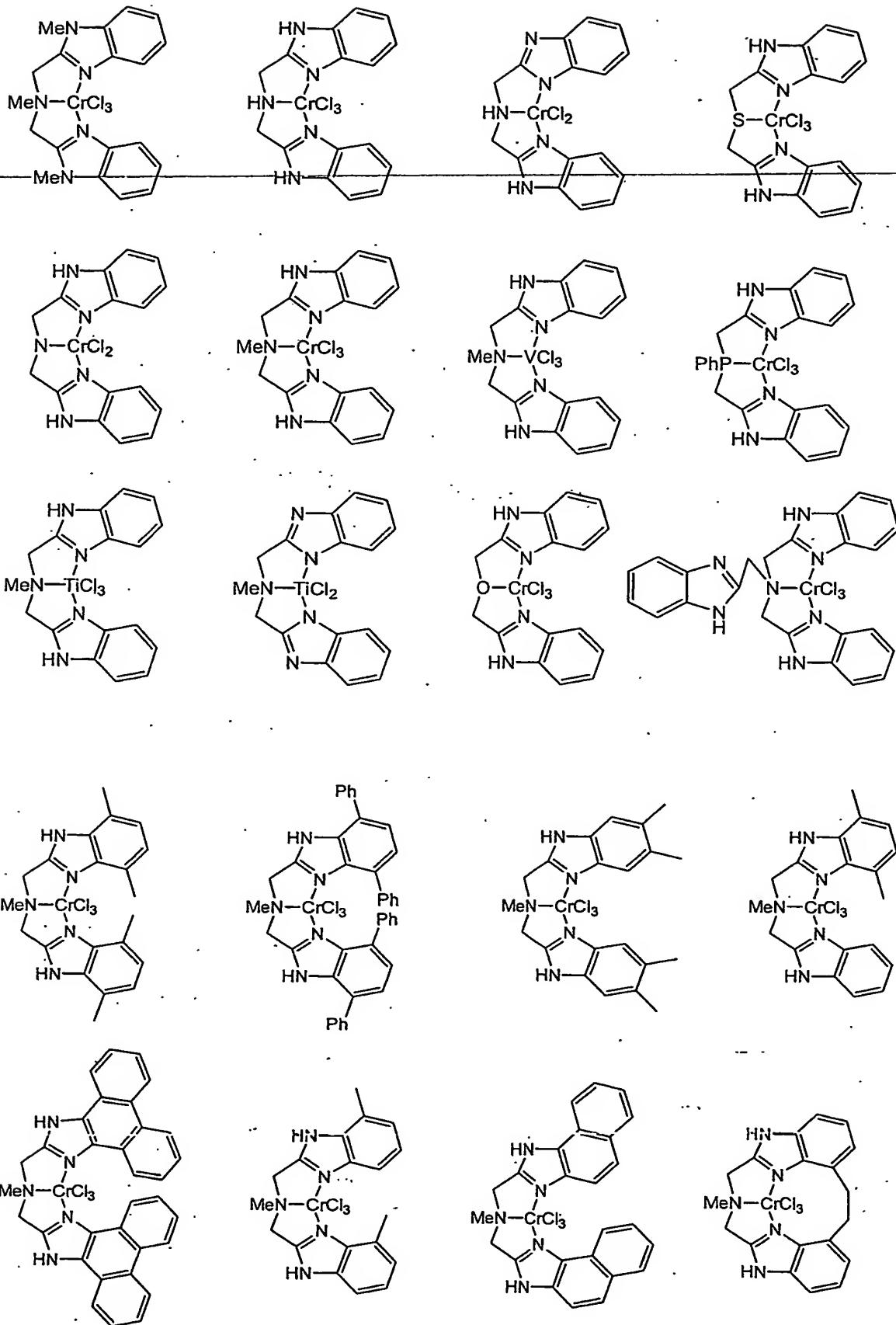
The catalyst of the present invention can, if desired, be utilised on a support material. Suitable support materials are, for example, silica, alumina, or zirconia, magnesia or a polymer or prepolymer, for example polyethylene, polystyrene, or poly(aminostyrene).

The following are examples of transition metal complexes that can be employed in the catalyst of the present invention:

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The catalysts of the present invention can if desired comprise more than one of the defined transition metal compounds.

In addition to said one or more defined transition metal compounds, the catalysts of the present invention can also include one or more other types of transition metal compounds or catalysts, for example, transition metal compounds of the type used in conventional Ziegler-Natta catalyst systems, metallocene-based catalysts, or heat activated supported chromium oxide catalysts (eg Phillips-type catalyst). The catalysts of the present invention may also be used in conjunction with other catalysts producing only 1-olefins, either inside or outside the polymerisation reactor, and in this way make copolymers of ethylene or propylene and these 1-olefins. Suitable catalysts for producing 1-olefins may produce only 1-butene, only 1-hexene or a distribution (for example, a Schulz-Flory distribution) of 1-olefins.

If desired the catalysts can be formed in situ in the presence of the support material, or the support material can be pre-impregnated or premixed, simultaneously or sequentially, with one or more of the catalyst components. The catalysts of the present invention can if desired be supported on a heterogeneous catalyst, for example, a magnesium halide supported Ziegler Natta catalyst, a Phillips type (chromium oxide) supported catalyst or a supported metallocene catalyst. Formation of the supported catalyst can be achieved for example by treating the transition metal compounds of the present invention with alumoxane in a suitable inert diluent, for example a volatile hydrocarbon, slurring a particulate support material with the product and evaporating the volatile diluent. The produced supported catalyst is preferably in the form of a free-flowing powder. The quantity of support material employed can vary widely, for example from 100,000 to 1 grams per gram of metal present in the transition metal compound.

The present invention further provides a process for the polymerisation and copolymerisation of 1-olefins, comprising contacting the monomeric olefin under polymerisation conditions with the polymerisation catalyst of the present invention.

Suitable monomers for use in making homopolymers using the polymerisation process of the present invention are, for example, ethylene, propylene, butene, hexene, and styrene. Preferred monomers are ethylene and propylene.

Suitable monomers for use in making copolymers using the polymerisation

process of the present invention are ethylene, propylene, 1-butene, 1-hexene, 4-methylpentene-1, octane, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, and styrene.

A particularly preferred process in accordance with the present invention is the copolymerisation of ethylene and/or propylene with comonomers selected from 1-olefins, acrylic acid esters, vinyl esters and vinyl aromatic compounds. Examples of suitable comonomers are 1-butene, 1-hexene, 4-methylpentene-1, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate, and styrene.

Preferred polymerisation processes are the homopolymerisation of ethylene or the homopolymerisation of propylene or copolymerisation of ethylene with one or more of propylene, butene, hexene-1 and 4-methylpentene-1 or copolymerisation of propylene with one or more of ethylene or butene.

The polymerisation conditions can be, for example, bulk phase, solution phase, slurry phase or gas phase. If desired, the catalyst can be used to polymerise ethylene under high pressure/high temperature process conditions wherein the polymeric material forms as a melt in supercritical ethylene. Preferably the polymerisation is conducted under gas phase fluidised or stirred bed conditions.

Slurry phase polymerisation conditions or gas phase polymerisation conditions are particularly useful for the production of high-density grades of polyethylene. In these processes the polymerisation conditions can be batch, continuous or semi-continuous. In the slurry phase process and the gas phase process, the catalyst is generally fed to the polymerisation zone in the form of a particulate solid. This solid can be, for example, an undiluted solid catalyst system formed from the complex A and an activator, or can be the solid complex A alone. In the latter situation, the activator can be fed to the polymerisation zone, for example as a solution, separately from or together with the solid complex. Preferably the catalyst system or the transition metal complex component of the catalyst system employed in the slurry polymerisation and gas phase polymerisation is supported on a support material. Most preferably the catalyst system is supported on a support material prior to its introduction into the polymerisation zone. Suitable support materials are, for example, silica, alumina, zirconia, talc, kieselguhr, or magnesia. Impregnation of the support material can be carried out by conventional techniques, for example, by forming a solution or

suspension of the catalyst components in a suitable diluent or solvent, and slurring the support material therewith. The support material thus impregnated with catalyst can then be separated from the diluent for example, by filtration or evaporation techniques.

In the slurry phase polymerisation process the solid particles of catalyst, or supported catalyst, are fed to a polymerisation zone either as dry powder or as a slurry in the polymerisation diluent. Preferably the particles are fed to a polymerisation zone as a suspension in the polymerisation diluent. The polymerisation zone can be, for example, an autoclave or similar reaction vessel, or a continuous loop reactor, e.g. of the type well known in the manufacture of polyethylene by the Phillips Process. When the polymerisation process of the present invention is carried out under slurry conditions the polymerisation is preferably carried out at a temperature above 0°C, most preferably above 15°C. The polymerisation temperature is preferably maintained below the temperature at which the polymer commences to soften or sinter in the presence of the polymerisation diluent. If the temperature is allowed to go above the latter temperature, fouling of the reactor can occur. Adjustment of the polymerisation within these defined temperature ranges can provide a useful means of controlling the average molecular weight of the produced polymer. A further useful means of controlling the molecular weight is to conduct the polymerisation in the presence of hydrogen gas which acts as chain transfer agent. Generally, the higher the concentration of hydrogen employed, the lower the average molecular weight of the produced polymer.

The use of hydrogen gas as a means of controlling the average molecular weight of the polymer or copolymer applies generally to the polymerisation process of the present invention. For example, hydrogen can be used to reduce the average molecular weight of polymers or copolymers prepared using gas phase, slurry phase or solution phase polymerisation conditions. The quantity of hydrogen gas to be employed to give the desired average molecular weight can be determined by simple "trial-and error" polymerisation tests.

Methods for operating gas phase polymerisation processes are well known in the art. Such methods generally involve agitating (e.g. by stirring, vibrating or fluidising) a bed of catalyst, or a bed of the target polymer (i.e. polymer having the same or similar physical properties to that which it is desired to make in the polymerisation process) containing a catalyst, and feeding thereto a stream of monomer at least partially in the

gaseous phase, under conditions such that at least part of the monomer polymerises in contact with the catalyst in the bed. The bed is generally cooled by the addition of cool gas (eg recycled gaseous monomer) and/or volatile liquid (eg a volatile inert hydrocarbon, or gaseous monomer which has been condensed to form a liquid). The

5 polymer produced in, and isolated from, gas phase processes forms directly a solid in the polymerisation zone and is free from, or substantially free from liquid. As is well known to those skilled in the art, if any liquid is allowed to enter the polymerisation zone of a gas phase polymerisation process the quantity of liquid is small in relation to the quantity of polymer present in the polymerisation zone. This is in contrast to
10 "solution phase" processes wherein the polymer is formed dissolved in a solvent, and "slurry phase" processes wherein the polymer forms as a suspension in a liquid diluent.

The gas phase process can be operated under batch, semi-batch, or so-called "continuous" conditions. It is preferred to operate under conditions such that monomer is continuously recycled to an agitated polymerisation zone containing polymerisation 15 catalyst, make-up monomer being provided to replace polymerised monomer, and continuously or intermittently withdrawing produced polymer from the polymerisation zone at a rate comparable to the rate of formation of the polymer, fresh catalyst being added to the polymerisation zone to replace the catalyst withdrawn from the polymerisation zone with the produced polymer.

20 When using the catalysts of the present invention under gas phase polymerisation conditions, the catalyst, or one or more of the components employed to form the catalyst can, for example, be introduced into the polymerisation reaction zone in liquid form, for example, as a solution in an inert liquid diluent. Thus, for example, the transition metal component, or the activator component, or both of these
25 components can be dissolved or slurried in a liquid diluent and fed to the polymerisation zone. Under these circumstances it is preferred the liquid containing the component(s) is sprayed as fine droplets into the polymerisation zone. The droplet diameter is preferably within the range 1 to 1000 microns. EP-A-0593083, the teaching of which is hereby incorporated into this specification, discloses a process for introducing a polymerisation 30 catalyst into a gas phase polymerisation. The methods disclosed in EP-A-0593083 can be suitably employed in the polymerisation process of the present invention if desired.

The present invention also provides a process for the oligomerisation and

cooligomerisation of 1-olefins, comprising contacting the monomeric olefin under oligomerisation conditions with the catalyst of the present invention.

Suitable monomers for use in making homooligomers using the oligomerisation process of the present invention are, for example, ethylene, propylene, butene, hexene, and styrene. The preferred monomer is ethylene.

Suitable monomers for use in making co-oligomers using the oligomerisation process of the present invention are ethylene, propylene, 1-butene, 1-hexene, 1-octene, 1-decene, 1-dodecene and further 1-olefins of the series C(n)H(2n) where n is an integer.

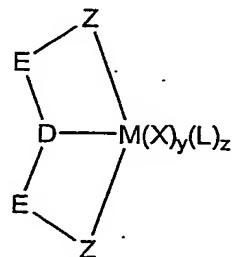
There exist a number of options for the oligomerisation reactor including batch, semi- batch, and continuous operation. The oligomerisation and co-oligomerisation reactions of the present invention can be performed under a range of process conditions that are readily apparent to those skilled in the art: as a homogeneous liquid phase reaction in the presence or absence of an inert hydrocarbon diluent such as toluene or heptanes; as a two-phase liquid/liquid reaction; as a slurry process where the catalyst is in a form that displays little or no solubility; as a bulk process in which essentially neat reactant and/or product olefins serve as the dominant medium; as a gas-phase process in which at least a portion of the reactant or product olefin(s) are transported to or from a supported form of the catalyst via the gaseous state. Evaporative cooling from one or more monomers or inert volatile liquids is but one method that can be employed to effect the removal of heat from the reaction. The (co-)oligomerisation reactions may be performed in the known types of gas-phase reactors, such as circulating bed, vertically or horizontally stirred-bed, fixed-bed, or fluidised-bed reactors, liquid-phase reactors, such as plug-flow, continuously stirred tank, or loop reactors, or combinations thereof. A wide range of methods for effecting product, reactant, and catalyst separation and/or purification are known to those skilled in the art and may be employed: distillation, filtration, liquid-liquid separation, slurry settling, extraction, etc. One or more of these methods may be performed separately from the (co-)oligomerisation reaction or it may be advantageous to integrate at least some with a (co-)oligomerisation reaction; a non-limiting example of this would be a process employing catalytic (or reactive) distillation. Also advantageous may be a process which includes more than one reactor, a catalyst kill system between reactors or after the final reactor, or an integrated

reactor/sePARATOR/purifier. While all catalyst components, reactants, inertS, and products could be employed in the present invention on a once-through basis, it is often economically advantageous to recycle one or more of these materials; in the case of the catalyst system, this might require reconstituting one or more of the catalystS

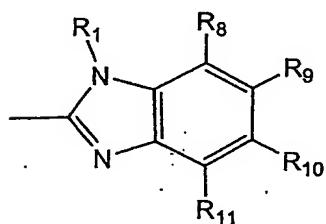
5 components to achieve the active catalyst system. It is within the scope of this invention that a (co)oligomerisation product might also serve as a reactant (e.g. 1-hexene, produced via the oligomerisation of ethylene, might be converted to decene products via a subsequent co-oligomermerisation reaction with two further ethylene units).

A further aspect of the present invention provides a novel transition metal

10 compound having the Formula



Z is specifically an imidazole-containing group of formula:



15 wherein R_1 , R_8 , R_9 , R_{10} and R_{11} are independantly hydrogen or a monovalent (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), and (vii) hydrocarbyl-substituted heteroatom groups. These defined groups preferably contain 1 to 30, more preferably 2 to 20, most preferably 2 to 12 carbon atoms. Examples of suitable aliphatic hydrocarbon groups are methyl, ethyl, ethylenyl, butyl, hexyl, isopropyl and tert-butyl. Examples of suitable alicyclic hydrocarbon groups are adamanyl, norbornyl, cyclopentyl and cyclohexyl. Examples of suitable aromatic hydrocarbon groups are phenyl, biphenyl, naphthyl, phenanthrenyl and anthacenyl. Examples of suitable alkyl substituted aromatic

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hydrocarbon groups are benzyl, tolyl, mesityl, 2,6-diisopropylphenyl and 2,4,6-triisopropyl. Examples of suitable heterocyclic groups are 2-pyridinyl, 3-pyridinyl, 2-thiophenyl, 2-furanyl, 2-pyrrolyl, 2-quinolinyl. Suitable substituents for forming heterosubstituted derivatives of said groups R₁ to R₁₁ are, for example, chloro, bromo, 5 fluoro, iodo, nitro, amino, cyano, ether, hydroxyl and silyl, methoxy, ethoxy, phenoxy (i.e. -OC₆H₅), tolyloxy (i.e. -OC₆H₄(CH₃)), xylyloxy, mesityloxy, dimethylamino, diethylamino, methylethylamino, thiomethyl, thiophenyl and trimethylsilyl. Examples 10 of suitable heterosubstituted derivatives of said groups (i) to (v) are 2-chloroethyl, 2-bromocyclohexyl, 2-nitrophenyl, 4-ethoxyphenyl, 4-chloro-2-pyridinyl, 4-dimethylaminophenyl and 4-methylaminophenyl. Examples of suitable hydrocarbyl-substituted heteroatom groups are chloro, bromo, fluoro, iodo, nitro, amino, cyano, 15 ether, hydroxyl and silyl, methoxy, ethoxy, phenoxy (i.e. -OC₆H₅), tolyloxy (i.e. -OC₆H₄(CH₃)), xylyloxy, mesityloxy, dimethylamino, diethylamino, methylethylamino, thiomethyl, thiophenyl and trimethylsilyl. Any of the substituents R₁ to R₁₁ may be linked to form cyclic structures. Substituents R₂ to R₁₁ may also suitably be inorganic groups such as fluoro, chloro, bromo, iodo, nitro, amino, cyano and hydroxyl.

Further suitable imidazole-containing groups may be obtained by removal of substituent R₁, for example by deprotonation when R₁ is hydrogen, to give formally monoanionic imidazole-containing groups.

20 R₁ is preferably hydrogen, an aliphatic hydrocarbon group, an aromatic hydrocarbon group or is removed to give a formally monoanionic benzimidazole group. R₈ to R₁₁ are preferably hydrogen, an aliphatic hydrocarbon group or an aromatic hydrocarbon group.

25 M is preferably a metal selected from Groups 3 to 7 of the periodic table, more preferably selected from Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn and most preferably V and Cr.

E is independently selected from divalent (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), and (vii) 30 hydrocarbyl-substituted heteroatom groups. Examples of suitable divalent group R₅ are -CH₂-, -CH₂CH₂-, -CH₂CH₂CH₂-, 1,2-phenylene, *trans*-1,2-cyclopentane, *trans*-1,2-cyclohexane, 2,3-butane, 1,1'-biphenyl, 1,1'-binaphthyl, and -Si(Me)₂-. It is preferred

that E is an aliphatic or aromatic hydrocarbon group. More preferably E is -CH₂CH₂-.

D is a donor group, for example oxygen, sulfur, an amine, an imine or a phosphine. Preferably D is oxygen, sulfur, an amine of formula -N(R₁₂)- or a phosphine of formula -P(R₁₃)- wherein R₁₂ and R₁₃ are hydrogen or (i) aliphatic hydrocarbon, (ii) alicyclic hydrocarbon, (iii) aromatic hydrocarbon, (iv) alkyl substituted aromatic hydrocarbon (v) heterocyclic groups, (vi) heterosubstituted derivatives of said groups (i) to (v), (vii) hydrocarbyl-substituted heteroatom groups and (viii) further imidazole-containing groups. Alternatively R₁₂ or R₁₃ may be removed, for example by deprotonation when they are hydrogen, to give a formally monoanionic fragments.

5 More preferably D is an amine of formula -N(R₁₂)- as defined above. R₁₂ is preferably hydrogen, an aliphatic hydrocarbon, an aromatic hydrocarbon or a further imidazole-containing group.

X is an anionic group and can be, for example, a halide, preferably chloride or bromide; or a hydrocarbyl group, for example, methyl, benzyl or phenyl; a carboxylate, for example, acetate or acetylacetate; an oxide; an amide, for example diethyl amide; an alkoxide, for example, methoxide, ethoxide or phenoxide. Alternatively, X can be a non-coordinating or weakly-coordinating anion, for example, tetrafluoroborate, a fluorinated aryl borate or a triflate. The anionic groups X may be the same or different and may independently be monoanionic, dianionic or trianionic.

20 L is a neutral donor group and can be, for example, a solvate molecule, for example diethyl ether or THF; an amine, for example, diethyl amine, trimethylamine or pyridine; a phosphine, for example trimethyl phosphine or triphenyl phosphine; or an olefin.

Values y and z are independently zero or integers such that the number of X and L groups satisfy the valency and oxidation state of the metal M. The value of y depends on the formal charge on each group Z and D, the charge on the anionic group X and the oxidation state of the metal M. For example, if M is chromium in oxidation state +3, both Z groups are neutral and D is neutral, then y is 3 if X is a monoanionic group (e.g., chloride); if M is chromium in oxidation state +3, one Z group is neutral, one Z group is monoanionic and D is neutral, then y is 2 if all X groups are monoanionic groups (e.g., chloride).

The invention is further illustrated with reference to the following Examples. In

the Examples all manipulations of air/moisture-sensitive materials were performed on a conventional vacuum/inert atmosphere (nitrogen) line using standard Schlenk line techniques, or in an inert atmosphere glove box.

Example 1a

Synthesis of N,N-bis(*1H*-benzimidazol-2-ylmethyl)-N-methylamine (1) A mixture of 4.0 g (27.2 mmol) methyliminodiacetic acid and 5.9 g (54.6 mmol) o-phenylenediamine in 20-30 ml ethyleneglycol was stirred at 190°C for 4 hours. After cooling to room temperature, the reaction mixture was mixed with 100-120 ml water and stirred for 15 minutes. The solid was filtered, washed with water (3 x 20 ml) and dried at 60°C under reduced pressure. Yield = 6.6 g (84%). The compound can be recrystallised from methanol/water mixture. ¹H NMR (250 MHz, d₆-DMSO), δ, ppm: 2.26 (s, 3H), 3.91 (s, 4H), 7.15 (br.s., 4H), 7.53 (br.s., 4H), 12.20 (v.br. s. 2H).

Example 1b

Synthesis of N,N,N-tris(*1H*-benzimidazol-2-ylmethyl)amine (2) A mixture of 3.5 g (18.2 mmol) nitrilotriacetic acid and 5.9 g (54.6 mmol) o-phenylenediamine in 30 ml ethyleneglycol was stirred at 190°C for 4h. Addition of 100 – 150 ml water to the cooled to room temperature reaction mixture afforded colourless bulky solid which was filtered, washed with 3 x 40 ml water and dried at 60°C at reduced pressure. recrystallisation from n-heptane gave 4.8 g (55%) of the desired product.

Example 1c

Synthesis of N-methyl-N,N-bis[(1-methyl-*1H*-benzimidazol-2-yl)methyl]amine (3) An amount of 1g (3.43 mmol) N,N-bis(*1H*-benzimidazol-2-ylmethyl)-N-methylamine in 30 ml THF was reacted with 0.33g (13.8 mmol) NaH for 30 min and then 0.43 ml (6.7 mmol) MeI were added. The reaction mixture was stirred for 4 hour at room temperature and 120 ml water were added. The solid was filtered, washed with water (3 x 20 ml) and dried at 60°C under reduced pressure. recrystallisation from methanol/water mixture gave 0.81 g (74 %) of the product. ¹H NMR (250 MHz, CDCl₃), δ, ppm: 2.39 (s, 3H), 3.67 (s, 6H), 3.93 (s, 4H), 7.20 – 7.30 (m, 6H), 7.68 (d, 2H).

Example 1d

Synthesis of N,N,N-tris[1-hexyl-*1H*-benzimidazol-2-yl)methyl]amine (4) A mixture of 2g (4.9 mmol) N,N,N-tris(*1H*-benzimidazol-2-ylmethyl)amine, 10 g anhydrous

K_2CO_3 , 20 ml DMF and 3.1 g (14.7 mmol) n-hexyliodide was stirred at room temperature for 48 hours. A volume of 200 ml water was added and the resulting mixture was intensively stirred for 30 min. The formed precipitate was filtered, washed with excess of water and dried at 60°C under reduced pressure. Recrystallisation from 5 n-heptane gave 2g (62 %) of the product. ^1H NMR (250 MHz, CDCl_3), δ , ppm: 0.44 (m, 6H), 0.73 (t, 9H), 0.82 (m, 6H), 0.97 (m, 6H), 1.14 (m, 6H), 3.42 (t, 6H), 4.22 (s, 6H), 7.22 (m, 9H), 7.74 (m, 3H).

Example 1e

Synthesis of N,N-bis[(1-methyl-*1H*-benzimidazol-2-yl)methyl]amine (5) A mixture 10 of 2.7 g (20.3 mmol) methyliminodiacetic acid and 5.0 g (40.6 mmol) N-methyl-o-phenylene diamine in 20-30 ml ethyleneglycol was stirred at 190°C for 4 hours. After cooling to room temperature, the reaction mixture was mixed with 100-120 ml water and stirred for 15 minutes. The solid was filtered, washed with water (3 x 20 ml) and dried at 60°C under reduced pressure. Yield – 3.5 g (56%). The compound can be 15 recrystallised from a methanol/water mixture.

Example 1f

Synthesis of N,N-bis(*1H*-benzimidazol-2-ylmethyl)amine (6) A mixture of 3.6 g (19.5 mmol) methyliminodiacetic acid and 4.9 g (45.3 mmol) o-phenylene diamine in 20-30 ml ethyleneglycol was stirred at 190°C for 4 hours. After cooling to room temperature, the 20 reaction mixture was mixed with 100-120 ml water and stirred for 15 minutes. The solid was filtered, washed with water (3 x 20 ml) and dried at 60°C under reduced pressure. Yield – 3.8 g (70.4%). The compound can be recrystallised from a methanol/water mixture.

Example 1g

Synthesis of N,N-bis(*1H*-benzimidazol-2-ylmethyl)-N-benzylamine (7) A mixture of 25 4.0 g (17.2 mmol) methyliminodiacetic acid and 3.9 g (36.1 mmol) o-phenylene diamine in 20-30 ml ethyleneglycol was stirred at 190°C for 4 hours. After cooling to room temperature, the reaction mixture was mixed with 100-120 ml water and stirred for 15 minutes. The solid was filtered, washed with water (3 x 20 ml) and dried at 60°C under 30 reduced pressure. Yield – 5.2 g (82%). The compound can be recrystallised from methanol/water mixture. ^1H NMR (250 MHz, d_6 -DMSO), δ , ppm: 3.73 (s, 2H), 3.94 (s, 4H), 7.26 (m, 7H), 7.48 (m, 6H), 12.4 (br.s, 2H).

Example 2

General procedure for the synthesis of chromium (III) complexes of the above ligands: A mixture of 15 mmol of the corresponding ligand and 15 mmol CrCl₃.3THF in 20 ml THF was stirred at 60°C for 10 min and at room temperature for 4 hours. The formed green solids were filtered, washed with THF and dried under vacuum.

Example 2a

Synthesis of {N,N-bis(*1H*-benzimidazol-2-ylmethyl)-N-methylamine}chromium trichloride (Cr1) This was synthesised according to the general procedure using compound (1) and CrCl₃.3THF and was obtained in 91% yield.

Example 2b

Synthesis of {N,N,N-tris(*1H*-benzimidazol-2-ylmethyl)amine}chromium trichloride (Cr2) This was synthesised according to the general procedure using compound (2) and CrCl₃.3THF and was obtained in 72% yield.

Example 2c

Synthesis of {N-methyl-N,N-bis[(1-methyl-*1H*-benzimidazol-2-yl)methyl]amine}chromium trichloride (Cr3) This was synthesised according to the general procedure using compound (3) and CrCl₃.3THF and was obtained in 67% yield.

Example 2d

Synthesis of {N,N,N-tris[1-hexyl-*1H*-benzimidazol-2-yl)methyl]amine}chromium trichloride (Cr4) This was synthesised according to the general procedure using compound (4) and CrCl₃.3THF and was obtained in 54% yield.

Example 2e

Synthesis of {N,N-bis[(1-methyl-*1H*-benzimidazol-2-yl)methyl]amine}chromium trichloride (Cr5) This was synthesised according to the general procedure using compound (5) and CrCl₃.3THF and was obtained in 51% yield.

Example 2f

Synthesis of {N,N-bis(*1H*-benzimidazol-2-ylmethyl)amine}chromium trichloride (Cr6) This was synthesised according to the general procedure using compound (6) and CrCl₃.3THF and was obtained in 79% yield.

Example 2g

Synthesis of {N,N-bis(*1H*-benzimidazol-2-ylmethyl)-N-benzylamine}chromium trichloride (Cr7) This was synthesised according to the general procedure using

compound (7) and CrCl₃.3THF and was obtained in 81% yield.

Example 2h

Synthesis of {N,N-bis(1*H*-benzimidazol-2-ylmethyl)-N-methylamine}vanadium trichloride (V1). A mixture of 0.25g (0.86 mmol) of (1) and 0.32g (0.86 mmol)

5 VCl₃.3THF was stirred in 15 ml tetrahydrofuran for 30 min at reflux. The reaction mixture was then left to cool to room temperature and stirred for 4 hours. The formed yellow-green precipitate was filtered, washed with 5 ml THF and dried under reduced pressure. Yield = 0.30 g (78%).

Example 2i

10 **Synthesis of [N,N-bis(1*H*-benzimidazol-2-ylmethyl)-N-benzylamine]Manganese dichloride (Mn7)** A mixture of 0.50 g (1.41 mmol) (7) and 0.18 g (1.41 mmol) MnCl₂ was stirred in 10 ml refluxing DCM for 10 min. The reaction mixture was then cooled to room temperature and stirred for another 4 hours. The pale pink precipitate was filtered, washed with 2 x 5 ml DCM and dried under reduced pressure. Yield 0.48 g (69

15 %).

Example 3

Ethylene oligomerisation and polymerisation tests: The ethylene oligomerisation/polymerisation reactions were performed under ethylene flow in a mechanically stirred Fischer-Porter glass reactor. After addition of 200 ml of toluene,

20 the corresponding scavenger and reactivator the reactor was stirred at room temperature for 5 - 10 minutes. A stock solution of the catalyst was prepared in the following way:

An amount of 0.5 – 10 mg of the corresponding catalyst precursor was dispersed in c.a. 10 – 50 ml toluene in a graduated Schlenk flask. Addition of the activator to the stirred suspension resulted in the immediate formation of a clear catalyst solution. An aliquot

25 of 1 ml was taken and added to the reactor, which was then quickly transferred and connected to the ethylene line. The oligomerisation/polymerisation reactions were

carried out for 1 hour unless otherwise stated and ethylene pressure of 4 bar. At the end of the run, the reactor was cooled to room temperature, the excess ethylene was vented off, and a sample was withdrawn and analysed for oligomers using GC. The reactor

30 content was then transferred to a baker, containing 400 ml methanol. The precipitated polymer was filtered, washed with methanol and dried at 60°C under reduced pressure.

The results are shown in Table 1.

Example	Catalyst (μ mol)	Activator (mmol)	T ($^{\circ}$ C)	Total Yield (g)	Activity g.mmol/h/bar	Yield oligomer (of total in g)	Comments
3a ¹	(Cr2) (20.0)	MAO (10.0)	20	22.	240	5	Oligomers 94% α -olefins
3b	(Cr1) (0.032)	MAO (3.6)	50	13	112400	3	Oligomers 95% α -olefins
3c	(Cr7) (10.0)	MAO (10.0)	20	48	1200	6	Oligomers 78% α -olefins
3d ²	(Cr6) (10.0)	MAO (10.0)	20	40	2000	14	Oligomers 81% α -olefins
3e	(Cr3) (19.0)	MAO (10.0)	28	25	330	12	Oligomers 87% α -olefins
3f ³	(V1) (2.0)	DEAC (0.46) EtOCOCCl ₃ (0.007)	50	10	3000	0	Mw 714000 Mn 157150 PDI 4.5

1 Run time 80 minutes

2 Run time 30 minutes

5 3 Run time 25 minutes

MAO = methyl aluminaoxane

DEAC = diethylaluminium chloride